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著者	末光 眞希
journal or publication title	Applied Physics Letters
volume	77
number	20
page range	3179-3181
year	2000
URL	<a href="http://hdl.handle.net/10097/47874">http://hdl.handle.net/10097/47874</a>

doi: 10.1063/1.1326037

# Mode transition between growth and decomposition of oxides on Si(001): Kinetically determined critical coverage for oxidation

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(Received 14 August 2000; accepted for publication 25 September 2000)

Effects of preoxidation on the reaction kinetics of oxygen molecules at Si(001) surface have been investigated by real-time ultraviolet photoelectron spectroscopy. A mode transition from decomposition to growth of surface oxides was found to exist at a certain initial oxide coverage, which is kinetically, not energetically, determined. By considering a change of balance between Si adatom and oxygen-monomer fluxes at the perimeter of oxide clusters, this mode transition is quantitatively described as a bifurcation of an autocatalytic-reaction rate equation. © 2000 American Institute of Physics. [S0003-6951(00)03346-5]

To respond to demands from recent ultrathin gate oxides in metal-oxide-semiconductor (MOS) devices, controls over surface reactions during Si thermal oxidation are of crucial importance. The importance is not limited to oxide growth, but possible oxide decomposition during oxidation should also be fully understood because it may have a significant relevance with the device performance. However, little knowledge is currently available concerning the interplay between growth and decomposition of oxides, though independent studies on either growth<sup>1-4</sup> or decomposition<sup>5-7</sup> have been rather extensive. In this letter, we describe our real-time ultraviolet photoelectron spectroscopy (UPS) measurement during dry (O<sub>2</sub>) oxidation of Si(001) surface, to show that a mode transition appears between oxide growth and decomposition depending on the initial oxide coverage. Furthermore, the mode transition is quantitatively described as a bifurcation of a nonlinear rate equation, the autocatalytic-reaction (ACR) model, which has been extended from its original application to Si oxidation<sup>4</sup> to include oxide decomposition. The physical background of this transition is argued from a change of balance between Si adatom and oxygen-monomer fluxes at the perimeter of oxide clusters.

Experiments were carried out using Ne I as an ultraviolet (UV)-light source to give the oxide coverage  $\theta$  in terms of the O 2*p* intensity. The experimental details including the real-time UPS system have been described previously.<sup>7</sup> The open circles in Fig. 1 show the time evolutions of the O 2*p* intensity obtained for oxidations at 700 °C, in which the initial oxygen pressure of  $5 \times 10^{-7}$  Torr was reduced to  $1 \times 10^{-7}$  Torr at either  $t = 150$  s (point A) or  $t = 200$  s (point B) of oxidation. We define the saturation oxide coverage under  $5 \times 10^{-7}$  Torr oxidation as one monolayer (ML). The oxygen irradiation at  $1 \times 10^{-7}$  Torr causes no oxidation when applied on a Si bare surface. This fact is consistent with the monotonic decrease of  $\theta$  in curve a, which starts from  $\theta$

$\approx 0.3$  ML. The situation is drastically changed when we delay the pressure reduction until  $\theta \approx 0.6$  ML, where the resultant curve (b) increases up to 1 ML even after the pressure reduction. Clearly, a critical value exists in the initial oxide coverage that separates the subsequent reaction kinetics between growth and decomposition of oxides. We would like to emphasize, however, that this critical coverage is determined from *kinetics*, not *energetics*. The finite saturation value at  $\sim 0.1$  ML in curve a, when compared with the fact that no oxidation occurs on clean Si surfaces at the same oxygen pressure, indicates that the equilibrium coverage varies with the history that the Si surface has experienced prior to the oxidation.

Kinetically controlled critical behaviors of this kind are best described by considering a relevant rate equation. The presence of the oxide decomposition in curve a suggests that the oxidation along curve b should also include oxide de-

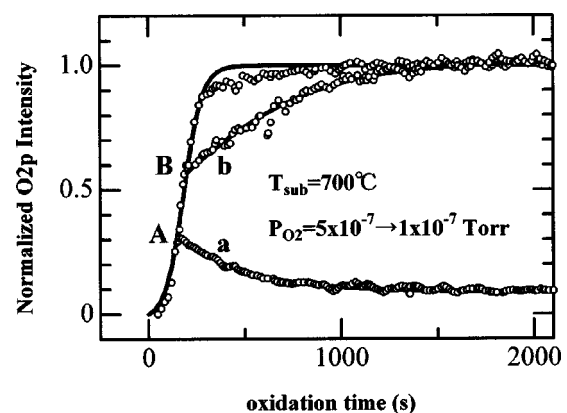


FIG. 1. Time evolutions of O 2*p* intensity during O<sub>2</sub> irradiation at 700 °C under oxygen pressure of  $5 \times 10^{-7}$  Torr, with (curves a and b) and without (the uppermost curve) related pressure reduction to  $1 \times 10^{-7}$  Torr. Without the pressure reduction, the time evolution shows a monotonic increase towards its saturation, which defines 1 monolayer (ML). No oxidation occurs when the reduced pressure ( $1 \times 10^{-7}$  Torr) is applied from the beginning. The time evolution after the pressure reduction is a delicate function of the initial oxide coverage; decaying down to 0.1 ML (curve a) when reduced at  $\theta = 0.3$  ML ( $t = 150$  s, point A) and increasing up to 1 ML when reduced at  $\theta = 0.6$  ML ( $t = 200$  s, point B). This behavior is quantitatively described as a bifurcation of the ACR equation, as shown in the solid lines.

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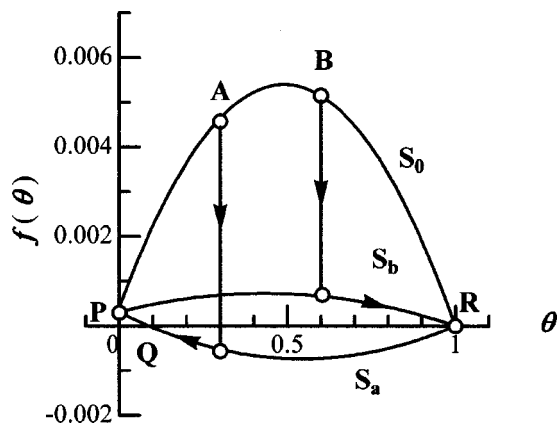


FIG. 2. Phase plots of the ACR equation used to fit the  $O_2p$  time evolutions in Fig. 1. The one for  $5 \times 10^{-7}$  Torr oxidation ( $S_0$ ) shows a positive, convex parabola, consistent with the monotonically increasing time evolution. The ones after the pressure reduction show a subtle, but a critical change in shape from concave ( $S_a$ ) to convex ( $S_b$ ) as the preoxidation duration increases.

composition. To describe time evolutions under such admixture of oxide growth and decomposition, we extend our ACR model developed for Si oxidations<sup>4</sup> to include oxide decomposition:

$$\frac{d\theta}{dt} = \frac{1}{\tau_g} (1-\theta)(\theta+\theta_g) - \frac{1}{\tau_d} \theta(1+\theta_d-\theta), \quad (1a)$$

$$= \left( \frac{1}{\tau_d} - \frac{1}{\tau_g} \right) \theta^2 + \left( \frac{1-\theta_g}{\tau_g} - \frac{1+\theta_d}{\tau_d} \right) \theta + \frac{\theta_g}{\tau_g} \equiv f(\theta). \quad (1b)$$

The subscripts  $g$  and  $d$  denote corresponding parameters of growth and decomposition, respectively. The first term in Eq. (1a) is identical with the one for pure oxidation,<sup>4</sup> while the second term for oxide decomposition has been introduced here by replacing the oxide coverage  $\theta$  in the first term with the Si bare portion  $1-\theta$ . That the latter term well describes the decomposition of 1 ML oxide has recently been confirmed by the authors.<sup>8</sup>

One of the largest benefits in employing the ACR formulation is that it has an analytical solution:

$$\theta(t) = \frac{\theta_1[\theta_2 - \theta(0)] + [\theta(0) - \theta_1]\theta_2 \exp\left(-\frac{\theta_2 - \theta_1}{\tau_1} t\right)}{\theta_2 - \theta(0) + [\theta(0) - \theta_1] \exp\left(-\frac{\theta_2 - \theta_1}{\tau_1} t\right)}. \quad (2)$$

Here,  $\theta_1$  and  $\theta_2$  are the roots of the equation  $f(\theta) = (\theta - \theta_1)(\theta - \theta_2)/\tau_1 = 0$ . The three solid lines in Fig. 1 are the fittings by Eq. (2), which all show excellent agreement with the experiment. In general, the temporal behavior of a solution for a nonlinear rate equation is best understood in terms of the phase plot, which is a parabola in the present ACR analysis. The three curves in Fig. 2 are the phase plots for the three fittings in Fig. 1. As we start with  $5 \times 10^{-7}$  Torr oxidation, the system departs from the point P along curve  $S_0$ . On reduction of the oxygen pressure, the system transfers from curve  $S_0$  down to curve  $S_a$  (point A) or to curve  $S_b$  (point B) depending on the timing. In the former case, the oxide coverage decreases after the pressure reduction towards point Q.

The finite  $\theta$  value of point Q ( $\sim 0.1$  ML) gives a good mathematical reasoning for the finite saturation of curve a in Fig. 1. In the latter case, the oxide coverage increases towards point R at  $\theta = 1$ . Equation (1b) indicates that the geometrical change of the phase plot from a convex to a concave is caused by a polarity change in the curvature  $1/\tau_d - 1/\tau_g \equiv 1/\tau_1$ , through variation of the parameters  $\tau_g$  and  $\tau_d$ . This is nothing but a bifurcation of a nonlinear rate equation. Within the framework of ACR formulation, therefore, the observed mode transition in the reaction kinetics of  $O_2/Si(001)$  system can be viewed as a bifurcation of the nonlinear ACR rate equation.<sup>9</sup>

What are the physical backgrounds for this change of  $1/\tau_1$ ? We notice here that there are two surface migrants on the Si surface that are responsible for growth and decomposition of oxides. The oxygen monomer, when attached to the perimeter of the oxide cluster, contributes to its growth.<sup>1</sup> The Si adatom, on the other hand, contributes to the oxide decomposition through the reaction  $Si + SiO_2 \rightarrow 2SiO(g)$ .<sup>5</sup> In our formulation, the former rate is represented by  $1/\tau_g$ , and the latter by  $1/\tau_d$ . If the Si adatoms' attacking dominates after weaker preoxidations and if the oxygen monomers' attaching dominates after heavier preoxidations, then the mode transition seen in Fig. 1 will be explained.

The validity of this idea is demonstrated by considering  $\theta$ -dependent migrant densities for both species. Using the BCF theory,<sup>10</sup> the migrant flux  $j_m$  attacking at the perimeter of the oxide cluster is given by

$$j_m = \frac{D_m}{x_m} (c_m^\infty - c_m^p) \tanh\left(\frac{L}{2x_m}\right) = j_m^0 \tanh\left(\frac{L}{2x_m}\right). \quad (3)$$

Here,  $D_m$  denotes the diffusion constant of the migrant  $m$  ( $m = O$  or  $Si$ ),  $x_m$  the diffusion length,  $L$  the mean intercluster distance,  $c_m^\infty$  the equilibrium migrant concentration in the absence of the oxide, and  $c_m^p$  the migrant concentration at the perimeter of the oxide cluster. Since  $\tanh(x) \approx 1$  for  $x > 1$ , the flux  $j_m$  is independent of  $L$  for  $L > 2x_m$ . This corresponds to a very initial oxidation. As the oxidation proceeds,  $L$  decreases to a point  $L < 2x_m$ , where  $j_m$  becomes proportional to  $L$  because  $\tanh(x) \approx x$  for  $x < 1$ . Unfortunately, little reliable data are available for the diffusion constant of oxygen atoms at Si surfaces. If we utilize the value for the bulk diffusion<sup>11</sup> after Engstrom *et al.*,<sup>1</sup>  $D_O$  is calculated to be  $1.51 \times 10^{-14}$  cm<sup>2</sup>/s at 700 °C. The mean life time of the surface oxygen monomer is estimated from the work by Yu *et al.*<sup>12</sup> to be 24.2 s for the same temperature. Using these values, the diffusion length  $x_O$  for oxygen monomer is calculated to be  $\sqrt{D\bar{t}} = 0.25$  nm. The diffusion length for Si adatoms is approximated as  $1/\sqrt{c_{Si}^\infty}$  if we assume a two-body nucleation.<sup>4</sup> Using the parameter values from Tromp *et al.*,<sup>13</sup>  $c_{Si}^\infty$  is estimated to be  $1.0 \times 10^{14}$  cm<sup>-2</sup>, which yields  $x_{Si} \approx 3.1$  nm. This situation,  $x_{Si} > x_O$ , permits a scenario in which the observed mode transition is explained using Eq. (3). In the early stage of the preoxidation, the intercluster distance  $L$  is much larger than the diffusion lengths:  $L/2 > x_{Si} > x_O$ . As the preoxidation proceeds,  $L$  begins to decrease to become  $x_{Si} > L/2 > x_O$ . At this stage, only the Si flux  $j_{Si}$  is decreased. By choosing proper values of  $j_{Si}^0$  and  $j_O^0$  under  $j_{Si}^0 > j_O^0$ , therefore, it is possible to reverse the initial order  $j_{Si} > j_O$  to  $j_{Si} < j_O$  during preoxidation. An example is

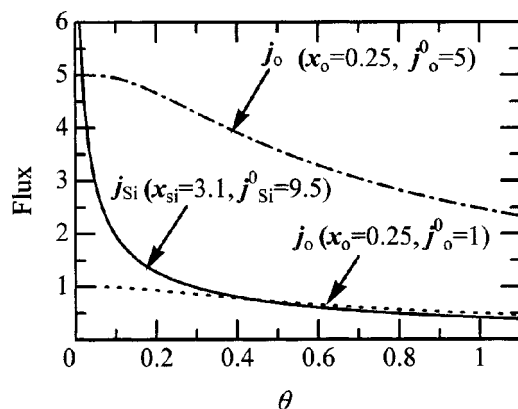


FIG. 3. Oxygen monomer flux  $j_o$  and the silicon adatom flux  $j_{si}$  at the perimeters of oxide clusters, calculated using the BCF theory (Ref. 10). With increase of the oxide coverage  $\theta$ , the fluxes begin to decrease when the mean intercluster distance  $L$  becomes less than  $2x_m$ , where  $x_m$  is the diffusion length of the migrant  $m$ . Using a likely assumption that  $x_{si} > x_o$ , it is demonstrated that  $j_o < j_{si}$  for  $\theta < 0.4$  ML and  $j_o > j_{si}$  for  $\theta > 0.4$  ML after the pressure reduction. This explains the observed growth/decay of the oxide clusters depending on the duration of the high-pressure oxidation.

shown in Fig. 3, in which we approximated  $L \cong \sqrt{1/N} - \sqrt{\theta/N} \cong a[(1 - \sqrt{\theta})/(1 - \theta)/\sqrt{\theta}]$  with  $N = (1 - \theta)^2 \theta / a^2$  ( $a = 0.543$  nm) being the number density of oxide clusters.<sup>4</sup> For the high pressure irradiation ( $j_{ox}^0 = 5$ , the dashed-dotted line),  $j_o > j_{si}$  for most of the  $\theta$  values, which simply indicates an oxidation. For the low pressure irradiation ( $j_{ox}^0 = 1$ , the solid line), the reaction mode becomes dependent on the peroxide coverage:  $j_o < j_{si}$  for  $\theta < 0.4$  and  $j_o > j_{si}$  for  $\theta > 0.4$ . Although actual reaction probabilities at the oxide perimeter may differ between the two migrants, this model at least demonstrates a possibility of explaining the observed mode transition in terms of the competitive reaction between the two migrants.

A technological importance of the oxide decomposition during Si thermal oxidation has been recently pointed out by

Takakuwa *et al.*<sup>14,15</sup> They argued the atomistic structure and the distribution of point defects at the SiO<sub>2</sub>/Si interface by considering the competition between the two processes. The present results provide a physicochemical and mathematical basis for our deeper understanding on the interplay between growth and decomposition of Si oxides, which will become even more important in further shrinkage of MOS devices and fabrication of Si nanostructures based on the Si thermal oxidation.<sup>16</sup>

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan.

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